PENTAERYTHRITOL TETRADODECANOATE (PETD) PRODUCTION: A STUDY ON THE EFFECTS OF TEMPERATURE AND OPERATING TIME OF REACTION

MOHD IKHWAN BIN YUSOF

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I declared that this thesis entitled "*Pentaerythritol Tetradodecanoate (PETD) Production: A study on the effects of temperature and operating time of reaction*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any degree.

Signature	: ……..
Name of Candidate	: MOHD IKHWAN BIN YUSOF
Date	: 27 NOVEMBER 2006

To my beloved family, especially to my mother. Thanks Allah S.W.T for blessing me.

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ABSTRACT

Pentaerythritol Tetradodecanoate (PETD) is a varnish additive that used in the magnetic wire coating. The esterification process is the main reaction in producing PETD. The raw materials to produce PETD are Pentaerythritol and Lauric Acid. The purification process of the raw materials is important before running the experiment to make sure the raw materials free from anything that debases, pollutes or contaminates. Sulfuric acid was used as a catalyst in the esterification between Pentaerythritol and Lauric acid. In this research, the thermodynamics study was carried based on the effect of operating and catalyst to the reaction. The dependent variables in the esterification to produce PETD are temperature and duration time of reaction. Otherwise, the independent variables are the amount of catalyst and reactants. This esterification was carried out at temperature between 180^{o}C to 270^{o}C and the duration time period of reaction between 8 hours to 24 hours. The reaction was conducted in the closed system batch reactor and the process was controlled in isothermal condition. The PETD that produced then was separated from water by using water distillation column. Then, the product was crystallized at the ambient temperature and the powder of PETD was obtained by crushing the crystal. The yield and color of the product were also observed. The product then was also analyzed using Thermogravimetric Analyzers (TGA). From the observation and analysis results, the optimum temperature and duration time of reaction was obtained at 220^{o}C for 16 hours. Then, the result from the analysis was compared with the standard, Senox 410.

ABSTRAK

Pentaerythritol Tetradodecanoate (PETD) adalah sejenis bahan pelindung yang digunakan di dalam lapisan wayar magnetik. Proces pengesteran adalah tindak balas utama yang digunakan untuk menghasilkan PETD. Bahan mentah yang digunakan untuk menghasilkan PETD adalah Pentaerythritol dan Asid Laurik. Proces penulenan atau pembersihan yang dilakukan pada bahan mentah adalah penting sebelum menjalankan eksperimen untuk memastikan bahan mentah tersebut bebas dari bahan tercemar atau kotor. Asid Sulfurik telah digunakan sebagai pemangkin di dalam tindak balas pengesteran diantara Pentaerythritol dan Asid Laurik. Di dalam kajian ini, kajian tentang termodinamik adalah berdasarkan kesan suhu tindak balas dan penggunaan pemangkin terhadap tindak balas. Pembolehubah bersandar di dalam pengesteran untuk menghasilkan PETD adalah suhu dan tempoh masa tindak balas. Manakala, pembolehubah tak bersandar adalah jumlah pemangkin dan bahan tindak balas. Tindak balas pengesteran ini berlaku pada suhu yang tinggi iaitu diantara 180 darjah Celcius hingga 270 darjah Celcius dan tempoh masa tindak balas diantara 8 jam hingga 24 jam. Tindak balas ini telah dijalankan di dalam sistem reaktor tertutup dan proces telah dikawal dalam keadaan isoterma. PETD yang terhasil kemudian telah dipisahkan daripada air dengan menggunakan proces penyulingan. Kemudian produk yang diperolehi telah dikristalkan pada suhu persekitaran dan serbuk PETD telah diperolehi dengan menghancurkan kristal tersebut. Jumlah hasil dan pemerhatian warna pada produk telah diperhatikan. Produk yang diperolehi kemudiannya telah dianalisis menggunakan Thermogravimetric Analyzers (TGA). Daripada pemerhatian dan keputusan analisis, suhu dan tempoh masa tindak balas yang optimum telah diperolehi iaitu pada 220 darjah Celcius untuk 16 jam. Kemudian, hasil daripada analisis yang dilakukan telah dibandingkan dengan yang telah sedia ada iaitu Senox 410.

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LIST OF ABBREVIATION

PETD	Pentaerythritol tetradodecanoate
LA	Lauric acid
PET	Pentaerythritol
H_2SO_4	Sulfuric acid
TGA	Thermogravimetric Analyzers

CHAPTER 1

INTRODUCTION

1.1 Introduction

Pentaerythritol Tetradodecanoate (PETD) is a varnish additive that used in the magnetic wire coating for a few years ago. Varnish additive is a finish applied to wood or other surfaces in order to provide a clear, hard, durable and protective finish. Besides that, there are many other applications of varnish such as an additive for paints. PETD is widely used by company in Malaysia such as Kaneka (M) Sdn. Bhd and Samsung. PETD was produced by Fischer esterification process. The raw materials used in esterification process are Lauric acid and Pentaerythritol.

Commonly, the optimum temperature and duration time of reaction for the reversible esterification process between Lauric acid with Pentaerythritol that produce PETD and water were investigated. This reaction of esterification occurs at higher temperature between 180^{o}C - 270^{o}C and at pressure of 1 atm. The reaction rate for the esterification is a function of process temperature. The reaction rate was increased with the increase of the operating temperature. The dependent variables in the esterification to produce PETD are temperature and duration time of reaction. Otherwise, the independent variables are the amount of catalyst and reactants. These variables were manipulated in the reaction to get the optimum product in terms of purity. In addition, the duration time period to produce PETD is between 8 hours to 24 hours. The reaction was conducted in the closed system batch reactor equipped with stirrer and condenser. The products that produced were analyzed using Thermogravimetric Analyzers (TGA).

Esterification is a general name for a chemical reaction between carboxylic acid with alcohol to produce an ester and water. Carboxylic acids react with alcohols to form esters through a condensation reaction. Esterification is a reversible reaction process occurred when all phases are in same equilibrium. Therefore, distillation process is an answer for esterification of PETD but it is not efficient because of limitation in equilibrium.

In this research, the thermodynamics study is an important to know about the thermodynamic variables, thermodynamic systems, and the effect of temperature to the reaction rate. The esterification of PETD is the new technology that already used in other country but not localized in Malaysia. So, the cost to import the PETD is very expansive from the others country.

1.2 Problem Statement

In this research, there are several problems that have been identified. The esterification of PETD is the new technology that already used in other country but not localized in Malaysia. So, the cost to import the PETD is very expansive from the outside. The challenge is to localize the production of PETD in our country in case to reduce the cost of import the PETD from others country. However, the local companies such as Kaneka (M) Sdn. Bhd and Samsung still has not known the technology to produce the PETD at an optimum output in terms of purity, production rate, energy consumption and process minimization.

The duration time of reaction to produce PETD is higher between 8 hours to 24 hours. In the industry such as Kaneka (M) Sdn Bhd, they produce PETD at the optimum duration time of 24 hours. Sulfuric acid was used commonly as the catalyst in the reaction in order to reduce the duration time period of reaction lower than 24 hours.

The temperature of reaction to produce PETD is high between 180˚C to 270˚C at 1atm. The energy needed for the esterification to produce PETD is higher. In the lab scale experiment to produce PETD, the problem is to maintain the temperature of the reaction at constant value. This is because the heat inside the heating medium was transferred to the surroundings.

The low purity of PETD was produced because the product still contains the small amount of Lauric acid and Pentaerythritol. That was most probably because the Lauric acid and Pentaerythritol not completely reacted with each other in the reaction. The small amount of the reactants that contained in the product must be reduced to get the higher purity of product. The stirrer was used in the reaction to make sure the reactants were completely reacting with each others.

1.3 Objective

The main objective of this research is to study the effects of temperature and catalyst application to the reaction to produce Pentaerythritol Tetradodecanoate (PETD).

1.4 Scope

In order to achieve the objective, four scopes have been identified in this research. The first scope is catalyst preparation. Sulfuric acid is very concentrated liquid and must be diluted with distilled water. This approach is important step before the catalyst mixed with reactants because the high concentrated catalyst can affect the purity of the product.

The second scope is the experimental set up. This experiment was conducted in closed system batch reactor equipped with stirrer and condenser. The heating

mantle used as the heating medium to heat the reaction in the reaction flask set. The distillation column was connected to reaction flask set to remove water from the reaction. The condenser with cooling water was connected to distillation column to condense the water. The receiving flask used to collect the water produced from the reaction. The stirrer was used to stir the mixture of the reactants.

The third scope is the experimental work. The experiments were running with different temperatures and duration time of reaction. Pentaerythritol and Lauric acid were mixed together in the batch reactor. Then, the mixture was heated by using heating mantle up to the temperature range between 180^{o}C to 270^{o}C. The temperature of the reaction will be manipulated at different value for different experiments that running. The reaction time of the experiment is between 8 hours to 24 hours. The optimum temperature will be investigated based on the reaction rate and the conversion of the product.

The last scope is the analysis product via Thermogravimetric Analyzers (TGA). TGA was used to analysis the composition of PETD that contained in the product. The type of TGA used to analysis the product is Q500.

CHAPTER 2

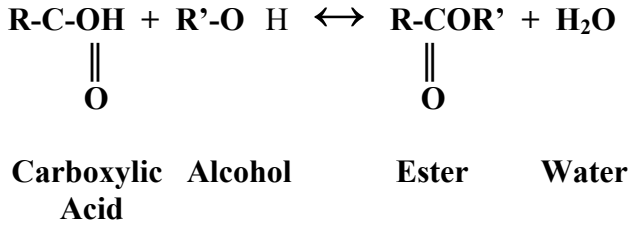
LITERATURE REVIEW

2.1 Esterification Process

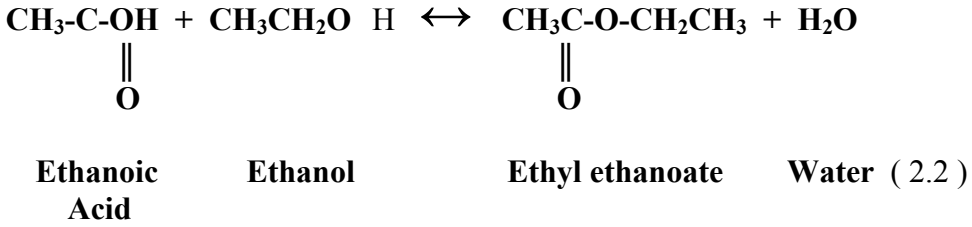
2.1.1 Introduction

Carboxylic acids react with alcohols to form esters through a condensation reaction known as esterification (Solomons and Fryhle, 2003). The alcohol and carboxylic acid react to form the ester and a water molecule. Esters were produced when carboxylic acids were heated with alcohols in the presence of an acid catalyst. The reactions proceed very slowly in the absence of strong acids (Solomons and Fryhle, 2003). Solomons and Fryhle also described that the reaction reach the equilibrium within a matter of a few hours when an acid and an alcohol are refluxed with a small amount of concentrated sulfuric acid. The Sulfuric acid was commonly used as the acid catalyst in the reaction. In organic chemistry, an acid catalyst is a compound that was used to donate protons. Usually this is done to create a more likely leaving group, such as converting an OH– to a H_2O. The ester was formed when dehydration occurs in the reaction. Since an esterification is equilibrium limited reaction, full conversion is not possible unless one of the products was removed (Nijhuis *et al*, 2002). Water that was produced in the reaction must be removed to keep the higher purity of product produced.

The equation for the general reaction between carboxylic acid, RCOOH and an alcohol, R'OH (where R and R' can be the same or different) is shown in Equation 2.1.



For simple example, we consider the esterification of ethyl ethanoate from ethanoic acid and ethanol shown in Equation 2.2.

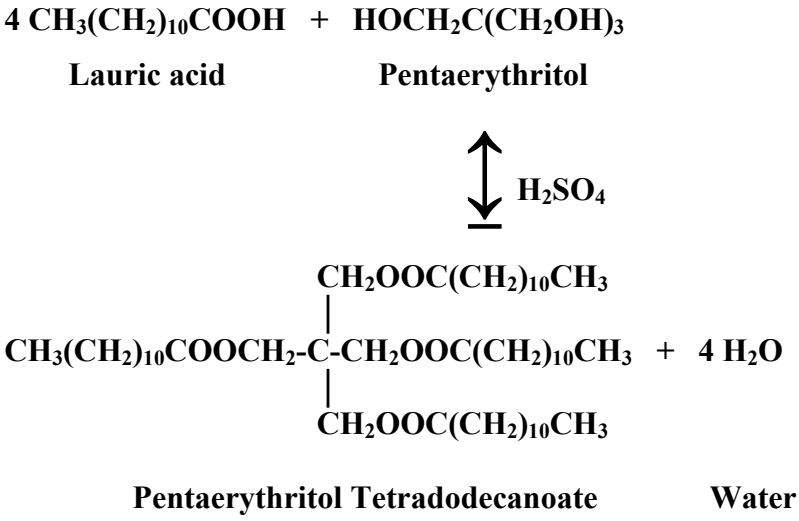


2.1.2 The simple esterification

In the esterification process, there is a simple esterification process to make an ester. Carboxylic acids and alcohols are often warmed together in the presence of a few drops of concentrated Sulfuric acid in order to observe the smell of the esters formed (Jim Clark, 2003). Because the reactions are slow and reversible, the ester that produced is lower in this time. The smell is often masked or distorted by the smell of the carboxylic acid. A simple way of detecting the smell of the ester is to pour the mixture into some water in a small beaker (Jim Clark, 2003). Esters are virtually insoluble in water and tend to form a thin layer on the surface. Excess acid and alcohol both dissolve and are tucked safely away under the ester layer. Small esters like ethyl ethanoate smell like typical organic solvents. Larger esters tend to form more slowly than the smaller ester (Jim Clark, 2003).

2.1.3 Esterification of Pentaerythritol Tetradodecanoate

The esterification of Pentaerythritol Tetradodecanoate (PETD) was produced from the reaction between Lauric acid and Pentaerythritol (Nurul Aini, 2005). Equation 2.3 shows the esterification reaction between Lauric acid and Pentaerythritol using Sulfuric acid as the catalyst (Eliefiyonna, 2005).



(2.3)

Equation 2.3 clearly shows that the esterification reaction between 1 mole of Lauric acid react with 4 moles of Pentaerythritol to produce 1 mole of PETD and 4 moles of water. Lauric acid is a medium-chain saturated fatty acid with 12 carbons and no double bonds which is also known as decanoic acid (Carey, 2000). Lauric acid has a systematic name of dodecanoic acid, a shorthand designation of $C_{12:0}$, and a molecular weight of 200.3 g/mol (Wu *et al*, 1995). Pentaerythritol is a tetrahydric neopentyl alcohol (Carey, 2000). It is an odorless white, crystalline, solid compound, non hygroscopic, practically non-volatile and stable in air. The Pentaerythritol is principally used in the surface coating industries (Kaewthong *et al*, 2003).

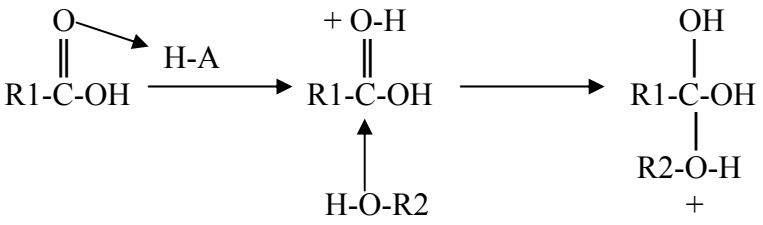
The purpose of using catalyst in the reaction is to lower down the temperature and duration time of the reaction. The reactions proceed very slowly in the absence of strong acids to reach equilibrium (Solomons and Fryhle, 2003). The production

reaction involving the mixture of Lauric acid and Pentaerythritol substrates occurred at the range between 150^{o}C to 300^{o}C (Kamal *et al*, 2005). In this research, the temperature range for the esterification reaction is higher between 180^{o}C to 270^{o}C. The higher temperature is needed for this reaction based on the melting point of Pentaerythritol which is the melting point is 260.5^{o}C. The duration time of reaction for producing PETD is higher between 8 hours to 24 hours (Kamal *et al*, 2005).

2.2 Fischer Esterification

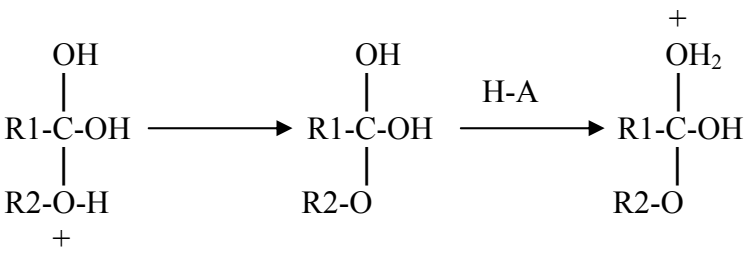
Fischer esterification is a special type of esterification and the process of forming an ester by refluxing a carboxylic acid and an alcohol in the presence of an acid catalyst as Scandium triflate as an acid catalyst (Solomons and Fryhle, 2003). Carboxylic acids are strong organic acids. Because acid-base reactions proceed rapidly, any nucleophile that is also a strong base will react with a carboxylic acid by removing a proton first before any nucleophilic substitution reaction can take place (Janice, 2006).

The general form of Fischer esterification mechanism was described is as follows:



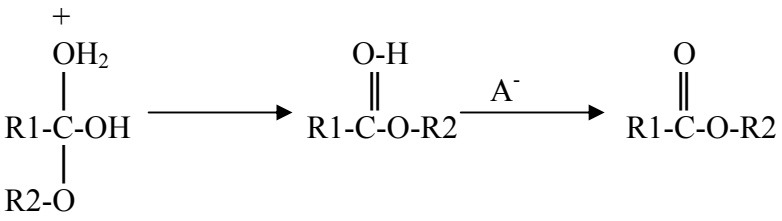
(2.4)

Equation 2.4 shows that the proton transfer from acid catalyst to carbonyl oxygen that was increased the electrophilicity of carbonyl carbon. Then the carbonyl carbon is then attacked by the nucleophilic oxygen atom of the alcohol and lead to the formation of an oxonium ion.



(2.5)

Equation 2.5 clearly shows that the proton transfer from the oxonium ion to a second molecule of the alcohol gives an activated complex. Then the proton transfers from one of the hydroxyl groups of the activated complex gives a new oxonium ion.

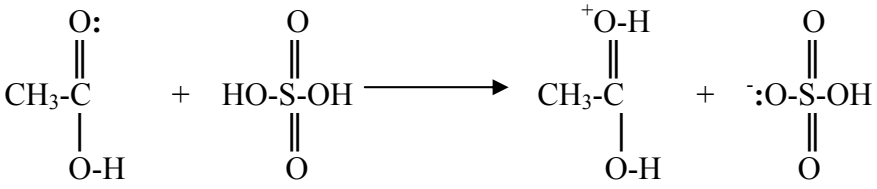


(2.6)

Equation 2.6 shows that the mechanism was followed by loss of water from the oxonium ion as electrons from the alcohol oxygen to form water and ester. Loss of a proton yields the ester.

For a typical example of Fisher esterification process, considered the formation of ethyl ethanoate from ethanoic acid and ethanol. Ethanoic acid reacts with ethanol in the presence of concentrated sulfuric acid as a catalyst to produce the ethyl ethanoate. The reaction is slow and reversible. In order to reduce the chances of the reverse reaction occurs, the ester was distilled off as soon as it was formed. All the steps in the mechanism are shown as one-way reactions because it makes the mechanism look less confusing. The reverse reaction is actually done sufficiently differently that it affects the way of the mechanism. The mechanism for the formation of ethyl ethanoate was described in detailed is as follows.

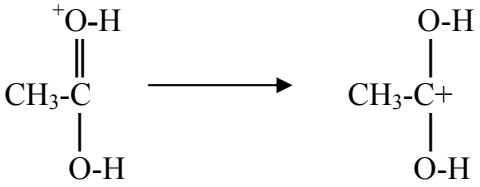
In the first step, the ethanoic acid takes a proton (a hydrogen ion) from the concentrated sulfuric acid. The proton becomes attached to one of the lone pairs on the oxygen which is double-bonded to the carbon as shown in Equation 2.7.



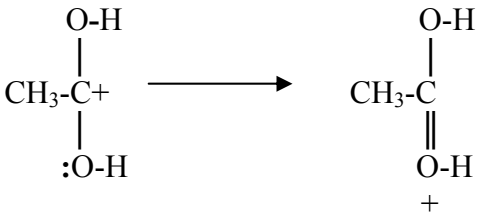
(2.7)

The transfer of the proton to the oxygen gave it a positive charge but it is actually misleading to draw the structure in this way.

The positive charge was delocalized over the whole of the right-hand end of the ion with a fair amount of positive on the carbon atom as shown in Equation 2.8.

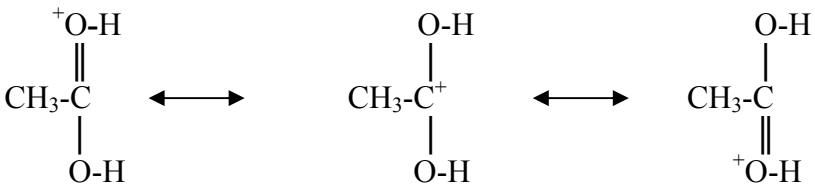


(2.8)



(2.9)

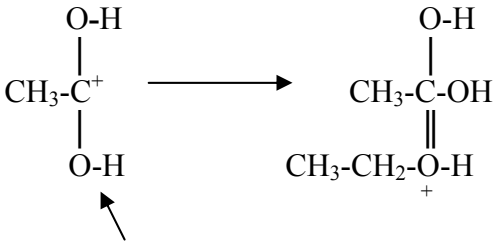
Equation 2.9 shows the way of writing the delocalized structure of the ion.



(2.10)

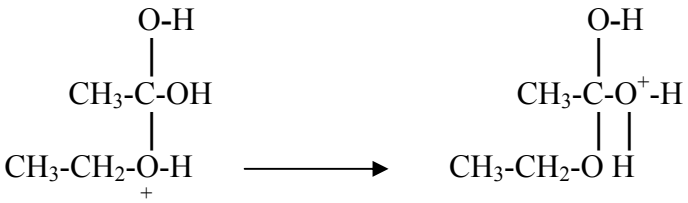
Equation 2.10 shows the double headed arrows described that each of the individual structures makes a contribution to the real structure of the ion. The various structures are known as resonance structures or canonical forms. There is some degree of positive charge on both of the oxygen atoms and also on the carbon atom. Each of the bonds between the carbon and the two oxygen will be the same that is somewhere between a single bond and a double bond.

Equation 2.11 shows the positive charge on the carbon atom was attacked by one of the lone pairs on the oxygen of the ethanol molecule.

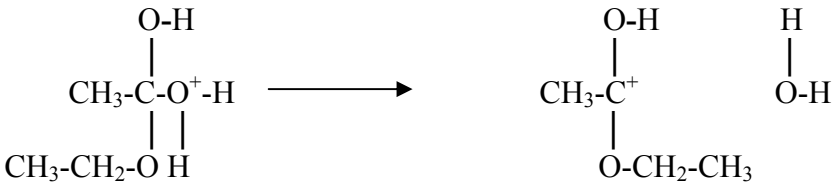


(2.11)

Equation 2.12 clearly shows that a proton (a hydrogen ion) was transferred from the bottom oxygen atom to one of the others. It gets picked off by one of the other substances in the mixture and then dumped back onto one of the oxygen more or less at random.



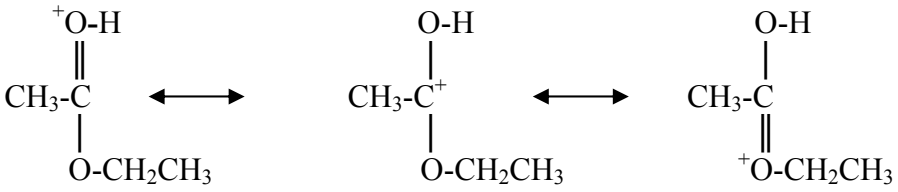
(2.12)



(2.13)

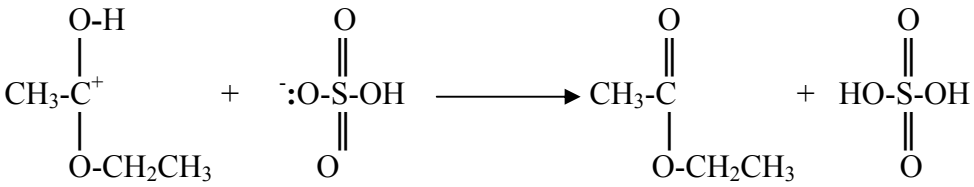
Equation 2.13 shows the molecule of water that was lost from the ion. The product ion has been drawn in a shape to reflect the products which are finally getting quite close to.

Equation 2.14 shows the structure for the latest ion. The positive charge is actually delocalized all over that end of the ion and there is also being contributions from structures where the charge is on the either of the oxygens:



(2.14)

Equation 2.15 shows that the hydrogen was removed from the oxygen by reaction with the hydrogensulphate ion which was formed way back in the first step.



(2.15)

The ester has been formed and the sulfuric acid catalyst has been regenerated.

2.3 Le Chatelier's Principle

Le Chatelier's principle states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change (Janice, 2006). Thus, removing a product from a reaction mixture as it is formed drives the equilibrium to the right, forming more products. The effect of different temperature to the reversible reaction was investigated. By using Le Chatelier's

principle, the change of temperature was affected the reaction. In the esterification between Lauric acid and Pentaerythritol, heat was absorbed during the reaction. Le Chatelier's principle can be used to favor products in dehydration reactions because the water product has a lower boiling point than the alcohol and carboxylic acid reactant. Thus, the water can be distilled from the reaction mixture as it is formed, leaving the alcohol and acid to react further, forming more product. For simple example, consider the following reaction in exothermic (heat is evolved):

$$A + 2B \longleftrightarrow C + D \qquad \Delta H = -250 \text{ kJ mol}^{-1} \qquad (2.16)$$

Equation 2.16 shows that 250 kJ was evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B. For reversible reactions, the value is always given as if the reaction was one-way in the forward direction. The back reaction (the conversion of C and D into A and B) would be endothermic by exactly the same amount.

According to Le Chatelier's principle, if the temperature of the reaction is increase, the position of equilibrium was moved in such a way as to counteract the change (Jim Clark, 2003). That means that the position of equilibrium was also moved so that the temperature was reduced again. If the system is in equilibrium at 300°C and the temperature was increased to 500°C. To cool down this temperature, it needs to absorb the extra heat in the reaction. The back reaction absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.

$$A + 2B \longleftrightarrow C + D \qquad \Delta H = -250 \text{ kJ mol}^{-1} \qquad (2.17)$$

The position of equilibrium moves to the left if the temperature is increase

If the condition was changed by decreasing the temperature, for example the system is in equilibrium at 500°C and the temperature was reduced to 400°C. The reaction tends to heat itself up again to return to the original temperature. The

position of equilibrium moves to the right. More A and B were converted into C and D at the lower temperature.

$$A + 2B \longleftrightarrow C + D \qquad \Delta H = -250 \text{ kJ mol}^{-1} \qquad (2.18)$$

The position of equilibrium moves to the right if temperature is decrease

As the conclusion, if the temperature of a system was increased in dynamic equilibrium favours the endothermic reaction. The system counteracts the change by absorbing the extra heat. If the temperature of a system was decreased in dynamic equilibrium favours the exothermic reaction. The system counteracts the change by producing more heat.

2.4 Thermodynamics study of esterification

2.4.1 Introduction

Thermodynamics (from the Greek thermos meaning heat and dynamis meaning power) is a branch of physics that studies the effects of changes in temperature, pressure and volume on physical systems (Cengel and Boles , 2002). The study of the laws that govern the conversion of energy from one form to another, the direction in which heat will flow, and the availability of energy to do work. It is based on the concept that in an isolated system anywhere in the universe there is a measurable quantity of energy called the internal energy (U) of the system. This is the total kinetic and potential energy of the atoms and molecules of the system of all kinds that can be transferred directly as heat; it therefore excludes chemical and nuclear energy. The value of U can only be changed if the system ceases to be isolated (Cengel and Boles, 2002). In these circumstances U can change by the transfer of mass to or from the system, the transfer of heat, or by work being done. One of the most fundamental laws of nature is the conservation of energy principle

(Smith *et al*, 2001). It states that during an interaction, energy can change from one form to another but the total amount of energy remains constant.

2.4.2 Effect of Temperature

The reaction rate constants for the esterification are a function of process temperature and were increased with the increase of the temperature (Liu and Chen, 2002). The accelerating of the reaction rate constant with the increase of the temperature for the forward reaction was faster than the backward process. So, water production rate was higher in a higher temperature than in a lower temperature. In this research, the temperature of the reaction is between 180^{o}C to 270^{o}C. The higher temperature was needed to the reaction between Lauric acid and Pentaerythritol to remove water in the higher quantity. Kinetic theory says that molecules are in constant motion (Jim Clark, 2003). The velocity of the molecules is directly proportional to the Kelvin temperature. The kinetic energy and molecule velocity increase with temperature. Reactions usually require collisions between reactant molecules or atoms (Jim Clark, 2003). The formation of bonds requires atoms to come close to one another. New bonds can form only if the atoms are close enough together to share electrons. Some collisions are not successful. These are called ineffective collisions. The particles simply hit and then rebound. Collisions that lead to products are called effective collisions. An effective collision must happen with a great enough speed, energy and force to break bonds in the colliding molecules. Collisions between molecules are more violent at higher temperatures (Smith *et al*, 2001). The higher temperatures mean higher velocities. This means there are less time between collisions. The frequency of collisions was increased. The increased number of collisions and the greater violence of collisions results in more effective collisions. The rate for the reaction increases. Reaction rates are roughly doubled when the temperature increases by 10 degrees Kelvin (Jim Clark, 2003). This means the rate can be quadrupled if the temperature was raised by 20 degrees Kelvin.

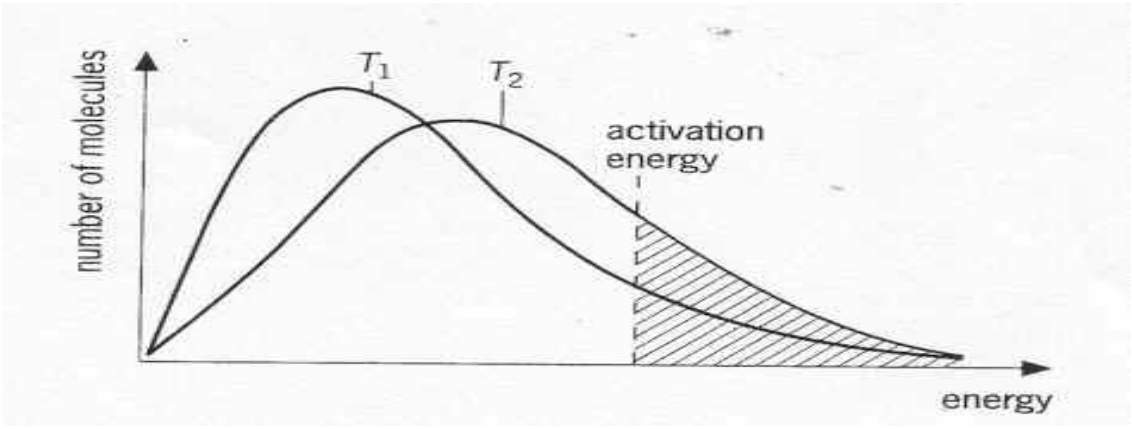


Figure 2.1: Graph number of molecules versus energy

The effect of temperature to the activation energy of reaction is shown in Figure 2.1. From the figure 2.1 above, two distribution curves are shown for a lower, T1 and higher temperatures,T2 and it was assumed that the area under the curve is the same for both temperatures i.e. the same number and population of molecules. Comparing lower temperature, T1 with higher temperature, T2 as the temperature increases, the peak for the most likely kinetic energy, KE was reduced and more significantly moves to the right to a higher value so there are more particles with the highest values of energy.

Now, consider the activation energy, E_a and the minimum KE the particles must have to react via e.g. bond breaking, the fraction of the population able to react at T1. However, at the higher temperature T2, the fraction with enough KE to react is given by the combined two areas under a curve of T1 and T2. Therefore, because of the shift in the distribution, at a higher temperature, a greater fraction of particles has the minimum KE to react. A relatively small change in temperature can have quite dramatic effect on the small, but significant, population of very high KE molecules; hence a relatively small change in temperature can significantly change the speed of a reaction. A reaction kinetic model was needed to describe the thermal reaction course over a wide temperature range (Bohm *et al*, 2000)

2.5 Effect of Catalyst

In the esterification process, the acid-catalyst was used to increase the reaction rate and to lower down the temperature of the reaction. If the reaction rate was increased, the duration time of the reaction to reach the equilibrium was also decreased. The energy needed for the reaction was also decreased because the lower activation energy of the reaction. The esterification process is both slow and reversible reaction (Solomons and Fryhle, 2003). The reaction was reached the equilibrium within a matter of a few hours when an acid and an alcohol were refluxed with a small amount of concentrated sulfuric acid or hydrogen chloride.

The variation of both forward and backward reaction rate occurred during the change of the concentrations of catalyst (Liu and Chen, 2002). The water production rate was higher for a higher concentration of catalyst since the forward reaction rate constant was higher than the backward one. The water contents in the reactor were higher for a higher concentration of catalyst for a period at the beginning during the reaction and then were lower later (Liu and Chen, 2002). Steric factors strongly affect the rates of acid-catalyzed hydrolysis of esters (Janice, 2006). Large groups near the reaction site, whether in the alcohol component or the acid component, slow both reactions markedly.

2.6 The separation process

The separation process known as distillation is a method for separating the various components of a liquid solution which depends upon the distribution of these components between a vapor phase and a liquid phase (Geankoplis, 2003). In this study, the reaction of PETD was produced in the batch reactor. The water that was produced in the batch reactor must be keep remove to get the best purity of product. The distillation process was used to keep remove water from the mixture. Distillation is a laboratory technique used for separating and purifying liquids. Distillation works by exploiting the different boiling temperatures of liquids

(Geankoplis, 2003). The more volatile liquid (the liquid with the lower boiling point) is typically evaporate first and the vapor will pass into a condensing column, where it can revert into a liquid (condense) on the cool glass where it trickles into a collection flask. Heating further was caused the less volatile liquids to evaporate and distill at higher temperatures. The two main kinds of distillation are simple distillation and fractional distillation, and both are used widely.

In the methodology of this research, a simple distillation apparatus consists of a boiling flask (reaction flask set) attached to an adapter holding a thermometer (to determine the boiling temperature of the liquid). The adapter connects to a condenser into which cold water is constantly passed through. The condenser leads into a collection flask for the purified liquid. Distillation is probably the most common technique for purifying organic liquids (Jim Clark, 2003). In simple distillation, a liquid was boiled and the vapors work through the apparatus until they reach the condenser where they were cooled and condense into liquid. Liquids were separated based upon their differences in boiling point (Geankoplis, 2003). Two important things to note, first is the tip of the thermometer must be correctly positioned slightly below the center of the condenser to accurately reflect the temperature of the vapors and second is the water supply should be connected to the lower port in the condenser and the drainage tube connected to the upper. Also be sure to use the thin-walled tubing and not the heavy walled vacuum tubing.

Fractional distillation is essentially the same as simple distillation except that a fractionating column was placed between the boiling flask and the condenser. The fractionating column is usually filled with glass or plastic beads. These beads improve the separation between the liquids being distilled. The reason that fractional distillation gives better separation between the liquids is because the glass beads in the fractionating column provide "theoretical plates" on which the refluxing liquid can condense, re-evaporate, and condense again, essentially distilling the compound over and over (Geankoplis, 2003). The more volatile liquids tends to push towards the top of the fractionating column, while lower boiling liquids were stayed towards the bottom, giving a better separation between the liquids. In an ideal situation, the temperature in the distillation flask would be equal to the boiling point of the mixture

of liquids and the temperature at the top of the fractionating column would be equal to the boiling point of the lower boiling compound; all of the lower boiling compound would be distilled away before any of the higher boiling compound. In reality, fractions of the distillate must be collected because as the distillation proceeds, the concentration of the higher boiling compound in the distillate being collected steadily increases.

In most esterification reactions, equilibrium was reached without conversion to a sufficient level (Izak *et al*, 2004). During reversible esterification, it is possible to shift the reaction towards higher product conversion by selective removal of reaction products from the reaction mixture. A promising way to improve conversion consists in coupling the esterification reaction with a pervaporation process (Izak *et al*, 2004). The yield of an esterification reaction can also be increased by removing water from the reaction mixture as it was formed (Solomons and Fryhle, 2003).

2.7 Thermogravimetric Analyzers (TGA)

2.7.1 Introduction

Thermogravimetry Analyzers (TGA) is thermal analytical procedures to determine changes in weight in relation to change in temperature. The technique involves monitoring the weight loss of the sample in a chosen atmosphere (usually nitrogen or air) as a function of temperature. Such analysis relies upon a high degree of precision in three measurements which are weight, temperature, and temperature change. TGA was commonly employed in research and testing to determine characteristics of materials such as polymers.

Gravimetric methods of analysis were based on the measurement of mass (Skoog *et al*, 2000). There are two major types of gravimetric methods there are

precipitation methods and volatilization methods. In precipitation methods, the analyte was converted to a sparingly soluble precipitate. This precipitate was then filtered, washed free of impurities and converted to a product of known composition by suitable heat treatment and the product was weighed. In volatilization methods, the analyte or its decomposition products were volatilized at a suitable temperature. The volatile product was then collected and weighed.

In this research, the type of TGA used to analysis the product is Q500 where the working temperatures range from 25^{o}C to 1000^{0}C. The thermal analysis can be performed in a controlled atmosphere including oxygen, nitrogen or helium with adjustable flow rates.

CHAPTER 3

METHODOLOGY

3.1 Introduction

In any activity that requires concrete results, a well-defined methodology for achieving those results is important. With a methodology, the process of achieving a result can be studied and the result verified. Without a methodology, this type of debugging and assurance is very difficult. In this research, the type of methodology is experimental method. The theoretical study is important to know about the overall process of methodology needed to run the experiment and how to analysis the data.

The overall process of research methodology is shown in Figure 3.1. This research methodology was divided into three stages. In the first stage, it involves the preparation of catalyst and experimental set up. For the second stage, after the suitable apparatus for experiment has been setup completely then the experimental work was continued. The final stage in this research methodology is analysis the product.

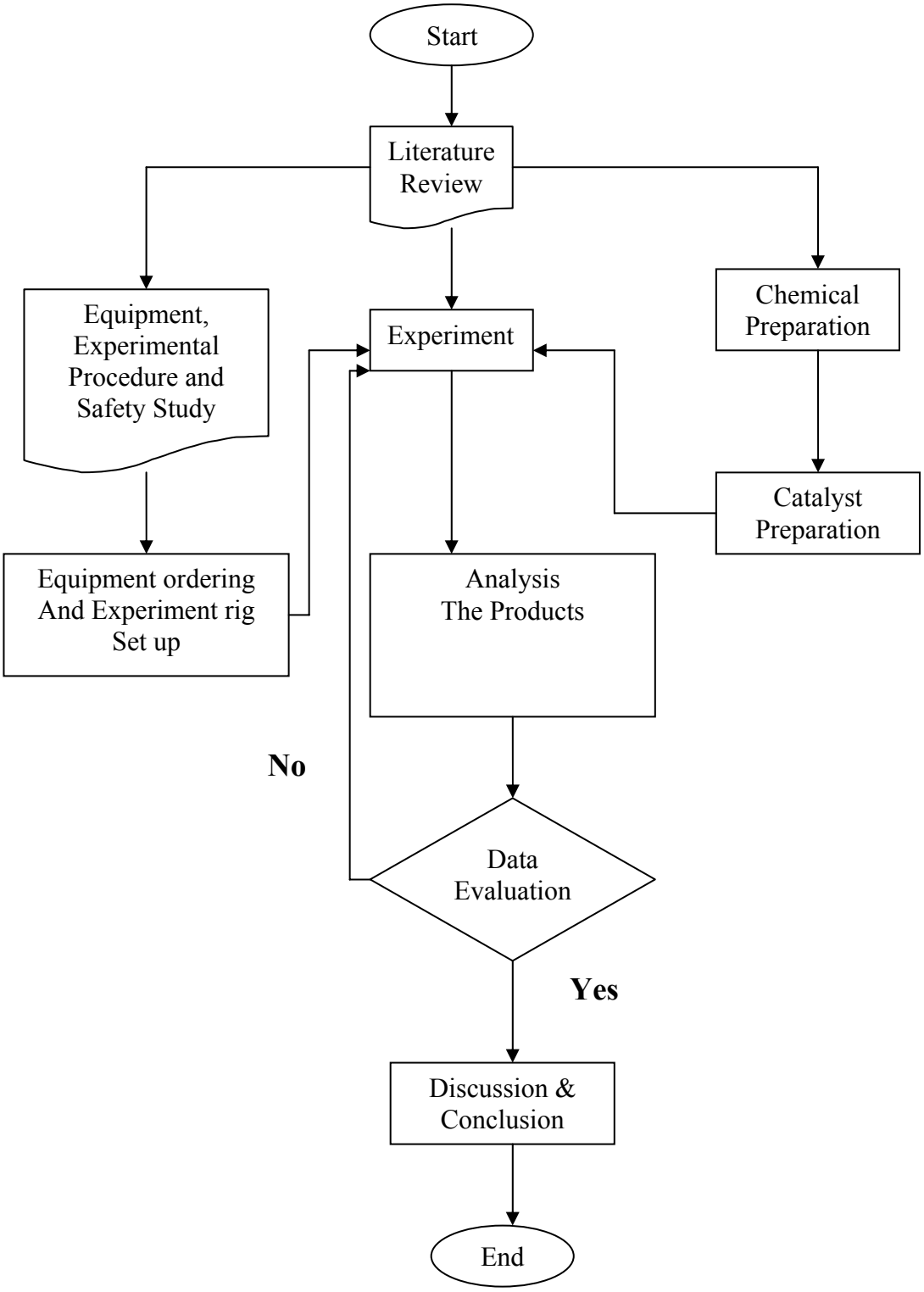


Figure 3.1: The process flow of methodology

3.2 Material

3.2.1 Raw Material Preparation

The raw materials used in this experiment were Pentaerythritol and Lauric acid. Pentaerytritol was supplied from Sigma Aldrich which has 98 % of purity. Meanwhile, Lauric Acid was supplied from Sigma Aldrich had a lower purity which is 95%. In this reaction, 1 mole of Pentaerythritol was reacted with 4 moles of Lauric acid to produce 1 mole of PETD and 4 moles of water. The mass ratio for the mixture between Pentaerythritol and Lauric acid was 1:4. In the reaction, 170.95 gram of Lauric acid and 29.05 gram of Pentaerythritol were mixed together in the reaction flask set. The total mass of the mixture was 200 gram.

3.2.2 Catalyst Preparation

Sulfuric acid was used as a catalyst in the esterification reaction between Pentaerythritol and Lauric acid. Sulfuric acid was supplied from ChemAR which has 95-98 % of purity. Before running the experiment, the catalyst was diluted with distilled water to 0.01mol of concentration. This was most probably because the higher concentration of Sulfuric acid was affected the purity of the product. In order to dilute the Sulfuric acid to 0.01mol, 0.4904 gram of Sulfuric acid was mixed with 500mL of distilled water in volumetric flaks.

3.3 Experimental Set Up

In producing the PETD, the esterification process was conducted in close system batch reactor. In setting up the apparatus, the lab scale experiment was used.

The example of schematic diagram for close system batch reactor was shown in Figure 3.2. This batch reactor was connected with simple distillation column for distillation process. In this research, the heating mantle was used as a heating medium and stirrer for stir the mixture of Lauric acid and Pentaerythritol. The mixture of the Lauric acid and Pentaerythritol was mixed together in the reaction flask set (500mL). A condenser was connected to distillation column to condense the water that was produced from the reaction. Cooling water was used in the condenser as a cooling agent. The water produced from the reaction was collected in the receiving flask. Digital thermocouple was used in the experiment to control and measure the temperature in the reaction flask set.

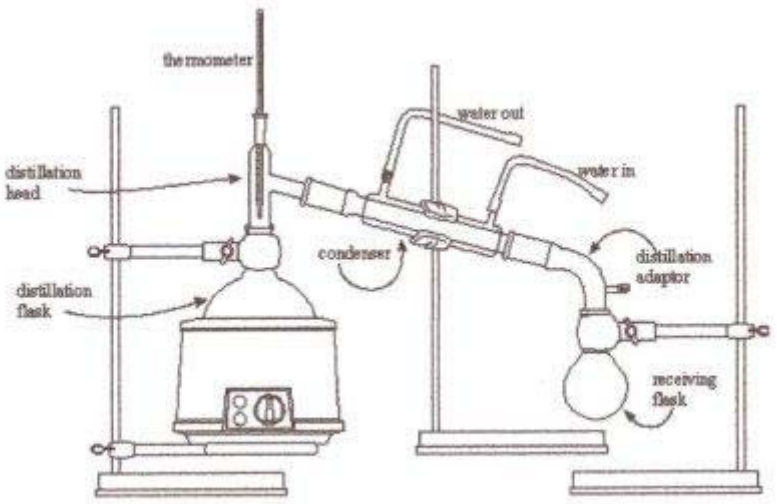


Figure 3.2: Simple batch distillation column

3.4 Experimental Work

Pentaerythritol and Lauric acid were mixed together in the batch reactor. Sulfuric acid as a catalyst had been put into the mixture. Then, the mixture was heated by using heating mantle up to the temperature range between 180^{o}C to 270^{o}C. The temperature of the reaction was manipulated at different value for different experiments that running. For the first experiment, the mixture was heated to 180^{o}C